HYDROGENATED CARBON–SILICON FILMS FABRICATED BY PACVD FROM TETRAMETHYLSILANE IN THE A.F. THREE-ELECTRODE REACTOR

J. Tyczkowski, K. Gubiec

Technical University of Łódź, Faculty of Process and Environmental Engineering,
Wolczanska 213, 93-005 Łódź, Poland
jatyczko@wipos.p.lodz.pl

A b s t r a c t. Amorphous hydrogenated carbon-silicon (a-Si_XC_Y:H) films were produced by plasma enhanced chemical vapor deposition (PECVD) in the audio-frequency (af) three-electrode reactor using tetramethylsilane as a source compound. The negative amplitude of af voltage, $V_{(-)}$, measured on a small electrode, on which the films were deposited, was the only operational parameter of the deposition process. Investigations of electrical conductivity, optical absorption and internal photoemission were carried out for the films deposited at various $V_{(-)}$. It was found that these films are composed of amorphous insulator (a-I) and amorphous semiconductor (a-S) fractions with different electronic structures. A basic band structure model for the a-I and a-S forms was proposed.

K e y w o r d s: audio-frequency glow discharge, carbon-silicon films, electronic structure.

INTRODUCTION

Numerous recent developments in advanced technology have drawn attention to amorphous materials produced in the form of thin films by plasma-assisted chemical vapor deposition (PACVD). A prominent place in their midst is occupied by hydrogenated carbon-silicon films (a-Si_XC_Y:H). Since the first report on their electronic properties [1], this material has witnessed considerably increase in research interest attributed primarily to its attractive electrical and optical properties, and consequently, to its technological applications, for example in solar cells [2].

Investigations performed thirteen years ago on the electrical and optical properties of a-Si_XC_Y:H films deposited from methylosilanes with varying methyl contents showed the first time that two specific groups of these films could exist. The first group was categorized as a typical amorphous semiconductor. On the contrary, the films ranked among the second group were characterized by the wide transport gap and long tails of localized states. It was also suggested that no

extended states occurred in this system; thus the electronic transport proceeded only by hopping. These films were called amorphous insulators [3].

The three-electrode reactor working at audio-frequency range of a glow discharge, constructed in 1993 [4], has turned out to be a very useful system for deposition of semiconducting and insulating films from the same single-source precursor and in the same deposition process. It has been found that these both groups of materials can be produced in the case of hydrogenated carbon-germanium (a-Ge_XC_Y:H) [5], carbon-tin (a-Sn_XC_Y:H) [6], and carbon-lead (a-Pb_XC_Y:H) films [7]. The energy of ions bombarding the growing films during the deposition is a factor that determines the kind of fabricated material. This energy is controlled by one of the deposition parameters, namely a coupling capacitance. A very small variation of this parameter in a defined range of its values causes step changes in the electronic properties of the films. On the other hand, the basic chemical structure of the films determined by chemical microanalysis, electron spectroscopies (ESCA and Auger), and IR spectroscopy, is practically unchanged when the step transition in the electronic structure occurs. This amazing phenomenon has been attributed to a transition between amorphous insulator (a-I) and amorphous semiconductor (a-S) states.

Investigations performed on a-Si_XC_Y:H films deposited in the three-electrode reactor have suggested that the a-I–a-S transition is also probable in this case [8,9]. In the present paper the results of electrical, photoelectrical and optical measurements for the a-I and a-S states of a-Si_XC_Y:H films are summarized and the basic energy level diagrams for both types of the films are proposed.

EXPERIMENTAL

The hydrogenated carbon-silicon films (a-Si_XC_Y:H), 0.2–0.5 μm thick, were plasma deposited from tetramethylsilane (TMS) in the three-electrode audio frequency reactor. Details concerning the reactor construction and its operation are described elsewhere [4]. Our reactor worked at a frequency of 20 kHz and with a voltage applied between the main electrodes of 2400 V (peak-to-peak). The only operational parameter of the deposition process was the negative amplitude $V_{(-)}$ of the a.f. voltage signal measured on the small electrode, on which the films were deposited. This amplitude, which is directly proportional to the impact energy of positive ions bombarding the growing film [4], was controlled by a variable capacitance coupling the small electrode with the powered main electrode, and was changed from 100 V to 1100 V. The flow rate and the initial pressure of TMS were selected in such a way to produce homogeneous and good adhered to a substrate films in the whole range of used $V_{(-)}$ and were 7.4 sccm and 17 Pa, respectively. As the substrate, 0.1 mm thick glass or quartz glass plates were used.

Measurements of electrical conductivity were carried out on samples in sandwich geometry for low-conducting films (conductivity lower than 10^{-10} S/m), and in coplanar geometry for high-conducting films (conductivity higher than 10^{-10} S/m). Current–voltage and current–temperature dependences were measured in vacuum (about 0.1 Pa). The specific conductivity was calculated from ohmic parts of the current–voltage characteristics. The activation energy of conductivity was determined in the temperature range from 295 to 350 K. Optical absorption measurements were performed by a transmission spectrophotometer in the wavelength range from 200 to 900 nm using samples prepared on quartz glass substrates. Internal photoemission investigations were performed according to the procedure described in Ref. [10,11]. These measurements were carried out in the 200–600 nm wavelength region, in air, using samples in sandwich geometry. The semitransparent top electrode of known transmittance was made of thermally evaporated Al, whereas the rear electrode was prepared from evaporated Au.

RESULTS AND DISCUSSION

Investigations of the electrical conductivity are the first step towards the characterization of the electronic properties. Figure 1(a) presents such results (the dark conductivity σ measured at room temperature) for the a-Si_XC_Y:H films deposited at various values of the parameter $V_{(-)}$. As one can see, two groups of the films exist, with very low (10^{-19}–10^{-16} S/m) and high (approx. 10^{-8} S/m) conductivity. A dramatic change by at least 8 orders of magnitude in σ occurs when $V_{(-)}$ is changed only by about 150 V (for $600 < V_{(-)} < 750$ V). With growing $V_{(-)}$ we also observe a decrease in the activation energy of the conductivity E_A (Fig. 1(b)). For the films with low conductivity E_A is between 0.8 and 0.5 eV while the group of high-conducting films is characterized by $E_A \approx 0.3$ eV.
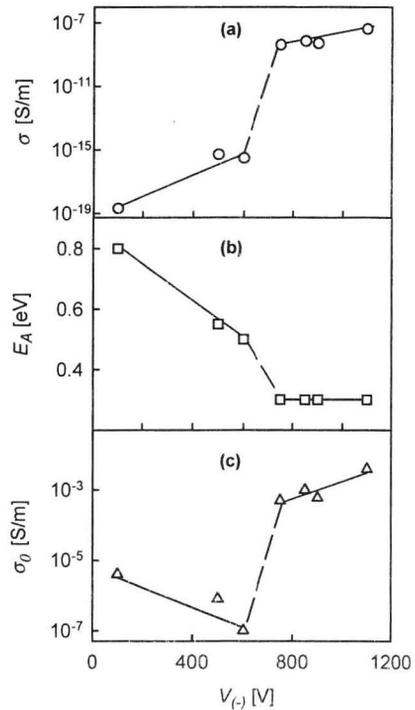

Fig. 1. Electrical conductivity of a-Si_XC_Y:H films as a function of $V_{(-)}$: (a) specific conductivity; (b) activation energy; (c) pre-exponential factor.

Taking the basic equation of the electrical conductivity:

$$\sigma = \sigma_0 \exp(-E_A / kT), \tag{1}$$

(where: k is the Boltzmann constant, and T is the tempe-rature), the pre-exponential factor σ_0 can be estimated. Its dependence on $V_{(-)}$ is presented in Fig. 1(c). For the group of low conducting films, σ_0 amounts to $5 \times 10^{-6} - 10^{-7}$ S/m and drastically increases up to 10^{-3} S/m when σ changes from the low to high conducting region. It is very probable that such a rise in σ_0 results from a change in the nature of transport processes, which can testify to the a-I–a-S transition taking place in this case [1,5].

The above suggestion is confirmed by the optical absorption measurements. Fig. 2 presents the absorption edges for three a-Si_XC_Y:H films deposited at $V_{(-)}$ = 1100 V, 500 V, and 100 V, drawn in the Tauc coordinate system, i.e. according to the following relation:

$$\alpha h v = B(h v - E_{OPT})^2, \tag{2}$$

where α is the absorption coefficient, $h v$ the energy of absorbed light, B the proportionality factor, and E_{OPT} the optical gap. Inspection of the figure reveals that two types of materials with evidently different E_{OPT} exist in the films. The film deposited at $V_{(-)}$ = 100 V (curve a) practically consists of one type of material (insulator) with E_{OPT} = 3.7 eV. On the other hand, the film produced at $V_{(-)}$ = 1100 V (curve c) can be recognized as the "pure" second type (semiconductor) with E_{OPT} = 2.3 eV. All films fabricated at an intermediate $V_{(-)}$ consist of the two types of hydrogenated Si-C alloy and their absorption edges are a superposition of absorption spectra belonging to the both types of the material. As an example, the absorption edge for film deposited at $V_{(-)}$ = 500 V is shown (curve b).

Taking the absorption edge for the pure semiconductor (curve c) and the part of the absorption edge for a given film where only absorption of the semiconducting fraction is observed (at $h v < 3.7$ eV) (see: curve b), the volume content of this fraction can be calculated. In Fig. 3, the semiconducting fraction content n_S is presented for all investigated films as a function of $V_{(-)}$. As one can see, n_S monotonically increases with the growing $V_{(-)}$. Comparing this dependence to those shown in Fig. 1, we can conclude that the a-I–a-S transition takes place when the semiconducting fraction makes at least 30 % of the film volume. The step change in σ and simultaneously the monotonic increase in n_S show clearly that the transition effect in the electrical properties of the a-Si_XC_Y:H films is connected with a percolation process. The estimated percolation threshold (approx. 30 %) corresponds to the theoretically calculated threshold for a mixture of insulating and conducting balls randomly close packed (27 %) [12].

Very interesting results and unassailable arguments confirming the fact that a-I and a-S types of a-Si_XC_Y:H films are fabricated in the three-electrode reactor, are provided by internal photoemission measurements. The investigations were

performed for two groups of the a-Si$_X$C$_Y$:H films: typical insulators (deposited at $V_{(-)} = 100$ V) and typical semiconductors ($V_{(-)} = 1100$ V).

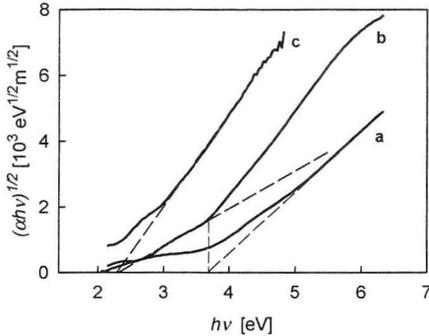**Fig. 2.** Optical absorption edges presented according to the Tauc relation for a-Si$_X$C$_Y$:H films deposited at various $V_{(-)}$: (a) 100 V; (b) 500 V; (c) 1100 V.

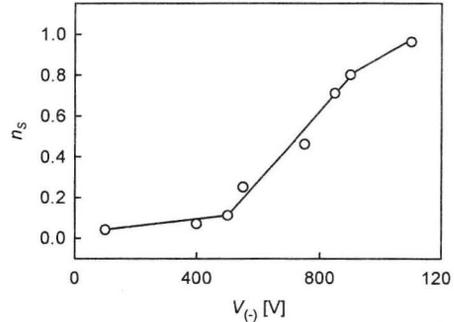**Fig. 3.** Semiconducting fraction content n_x in the a-Si$_X$C$_Y$:H films as a function of $V_{(-)}$.

In the both cases the barrier heights for electrons and holes injected from the metal electrodes have been determined according to the Fowler relation [13]:

$$Y \propto (h\nu - \Phi)^2, \tag{3}$$

where Y is the photocurrent quantum yield, $h\nu$ is the exciting photon energy, and Φ is the contact barrier height (for electrons or holes). A typical Fowler's plot for the insulating films is presented in Fig. 4. In this case, for positive polarization on the rear Au electrode, electrons are photoinjected from the top Al electrode whereas the Au electrode delivers holes (the film is transparent in the whole range of the exciting light). The measurements performed for various voltages applied to the sample and various directions of the polarization have shown that: (*1*) very high density of surface states exists in the contacts of a-I–metal (Al or Au), and (*2*) the contact barrier height Φ (for both electrons and holes) depends linearly on the square root of the applied voltage U, according to the Schottky relation [13]:

$$\Phi = \Phi_0 - \beta (U/d)^{1/2}, \tag{4}$$

where Φ_0 is the barrier height for $U = 0$, d is the film thickness, and β is the Schottky coefficient. The average value of the coefficient β is 3×10^{-5} eV(m/V)$^{1/2}$, which is a typical value for insulating carbon-silicon films [14].

For the semiconducting films, the internal photoemission process proceeds in a different way than that characteristic of the insulating films. Typical Fowler's plots for electrons and holes photoinjected to the a-S films are shown in Fig. 5. In this case we can observe the injection of charge carriers only from the top Al electrode (the films are non-transparent for the exciting light). Also, the

dependence of the barrier heights on the applied voltage is completely different. For the electron injection a linear relation of $\Phi \propto U$ is found whereas for the hole injection a relation of $\Phi \propto U^{1/2}$ appears. These results are indicative of a typical semiconducting type of the investigated material [10].

Different electronic (electrical and optical) properties and different photoinjection processes make irrefutable evidence of the fact that two qualitatively different, from the electronic structure point of view, types of a-Si$_X$C$_Y$:H films are fabricated. Taking the results of the electrical conductivity and the internal photoemission measurements, a band structure model for both a-I and a-S forms of the a-Si$_X$C$_Y$:H films can be proposed [9,10]. Such a model in the form of the energy level diagrams for the region of the film–metal contacts is presented in Fig. 6. In both cases the intrinsic p-type conductivity is assumed. The most striking difference between the both structures manifests itself in values of the transport gap, which amount to 6.8 and 3.7 eV for a-I and a-S, respectively. Detailed analysis of the electronic structure of the a-I and a-S fractions as well as the interaction of these fractions in the a-Si$_X$C$_Y$:H films are the aim of the further investigations.
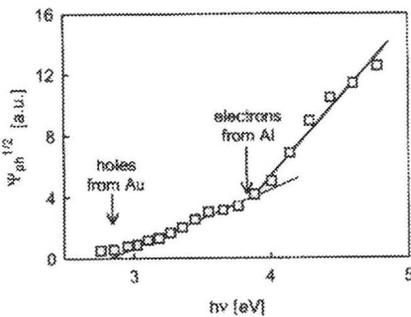

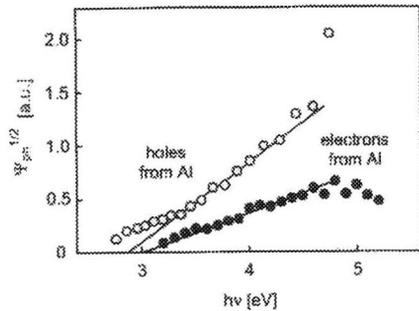**Fig. 4.** Fowler's diagram for the a-Si$_X$C$_Y$:H insulating films.

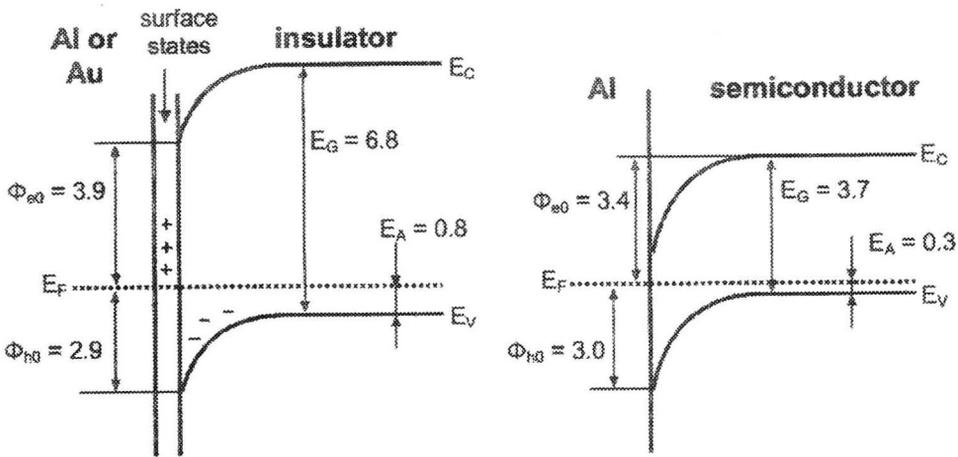**Fig. 5.** Fowler's diagram for the a-Si$_X$C$_Y$:H semiconducting films.

Fig. 6. Band structure models for insulating and semiconducting a-SiXCY:H films in the region of the film–metal contacts. All values are given in eV.

CONCLUSIONS

The results presented in this work have proved that the a-Si_XC_Y:H films deposited from tetramethylsilane in the three-electrode reactor can be obtained as insulating or semiconducting materials. The transition from insulating to semiconducting films is controlled by a percolation process and takes place when the a-S fraction content attains approximately 30 % of the whole volume of the film. It has been also shown that the a-I and a-S fractions of the a-Si_XC_Y:H differ fundamentally in the electronic structure and, in consequence, in electronic properties such as the electrical conductivity and the optical absorption.

The existence of two qualitatively different types of a-Si_XC_Y:H films is a very exciting phenomenon not only from the basic research point of view. This also offers new possibilities for thin film technology consisting in preparation of a novel class of layer structures formed from twin films of the a-Si_XC_Y:H insulator and semiconductor deposited from the same single-source precursor and in the same deposition process.

REFERENCES

1.   **Anderson D.A., Spear W.E.**, Phil. Mag. B 35 (1977) 1.
2.   **Luft W., Tsuo Y.S.**, Hydrogenated Amorphous Silicon Alloy Deposition Processes, Marcel Dekker, New York, 1993.
3.   **Tyczkowski J.**, Thin Solid Films 168 (1989) 175.
4.   **Tyczkowski J.**, J. Vac. Sci. Technol. A 17 (1999) 470.

5. **Tyczkowski J., Kazimierski P.**, J. Phys. D: Appl. Phys. 27 (1994) 179.
6. **Tyczkowski J., Pietrzyk B., Hatanaka Y., Nakanishi Y.**, Appl. Surf. Sci. 113/114 (1997) 534.
7. **Tyczkowski J., Pietrzyk B., Delamar M.**, Chem. Mater. 10 (1998) 3879.
8. **Tyczkowski J., Kazimierski P., Odrobina E.**, Surf. Coat. Technol. 60 (1993) 609.
9. **Tyczkowski J., Pietrzyk B., Kazimierski P., Gubiec K.**, Surf. Coat. Technol. 142/144 (2001) 843.
10. **Tyczkowski J., Odrobina E., Gazicki M., Olcaytug F.**, J. Non-Cryst. Solids 137/138 (1991) 875.
11. **Tyczkowski J., Ledzion R.**, J. Appl. Phys. 86 (1999) 4412.
12. **Zallen Z.**, The Physics of Amorphous Solids, John Wiley and Sons, New York, 1983, Chap. 4.
13. **Kao K.C., Hwang W.**, Electrical Transport in Solids, Pergamon Press, Oxford, 1981, Chaps. 2 and 6.
14. **Yasuda H.**, Plasma Polymerization, Academic Press, Orlando, 1985, Chap.11.

WARSTWY SZKLIW KRZEMOWĘGLOWYCH WYTWARZANE W PROCESIE PACVD Z TETRAMETYLOSILANU W A.F. REAKTORZE TRÓJELEKTRODOWYM

J. Tyczkowski, K. Gubiec

Wydział Inżynierii Procesowej i Ochrony Środowiska, Politechnika Łódzka,
90-924 Łódź, Wolczańska 215, Polska
jatyczko@wipos.p.lodz.pl

S t r e s z c z e n i e. Amorficzne warstwy szkliw krzemowowęglowych (a-Si_XC_Y:H) otrzymywano w trójelektrodowym reaktorze af plazmy (proces PECVD) używając jako surowca tetrametylosilanu. Badania przewodnictwa elektrycznego, absorpcji światła i wewnętrznej fotoemisji, przeprowadzone przy różnych wartościach $V_{(-)}$ (ujemnej amplitudy napięcia), jedynego parametru umożliwiającego sterowanie procesem, wykazały obecność frakcji typu izolatora i półprzewodnika. Otrzymanie takich materiałów otwiera nowe możliwości przed zastosowaniami cienkich warstw szkliw plazmowych.

S ł o w a   k l u c z o w e : AF wyładowania świetlące, warstwy krzemowowęglowe, struktury elektronowe.